

DENSE Ce³⁺-ACTIVATED SCINTILLATOR MATERIALS

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ABSTRACT

Several very dense hosts for Ce³⁺ are identified and their scintillation characteristics at 300 K are reported. Included are simple oxides, aluminates, borates, tantalates, BGO, and fluorides.

INTRODUCTION

Cerium-activated scintillator materials have received renewed interest for many applications because of the favorable spectroscopic properties of Ce³⁺ and the ability to incorporate Ce³⁺ into many different host materials.[1] Many of these materials combine high light yield, favorable emission wavelength, fast fluorescence decay, and temperature stability which make them attractive for use in detectors for high energy physics [2] and medical imaging.[3] Whereas the former application is tolerant regarding light output, the latter requires the highest scintillation efficiency. High density and good stopping power are important for both applications. Cerium-activated materials with increasingly higher densities have been developed in recent years, lutetium-based compounds being of particular current interest. We have used crystal diffraction databases [4] to identify potential hosts for Ce³⁺ having densities in the range $\sim 7\text{-}10\text{ g/cm}^3$. Here we present preliminary results for several very dense Ce-activated materials. Samples were generally powders or polycrystalline materials. All scintillation measurements were performed at room temperature using a pulsed x-ray apparatus and techniques described elsewhere.[5] Decay kinetics are reported but luminescence spectra have not been characterized. At this stage our intent is to survey and screen those materials operating at room temperature that warrant further spectroscopic studies and growth efforts; optimized cerium concentration, precise measurements of scintillation light output, or studies of other important properties such as radiation damage, afterglow, etc. have thus not been made.

LUTETIUM OXIDES

The properties of three lutetium oxide compounds are listed in Table 1. Since for applications such as PET a large photoelectric fraction is desirable, the photoelectric length (attenuation length divided by photoelectric fraction) for 511 keV photons is given. Simple Lu₂O₃ is a very dense material, but preparation of single crystals is difficult because of the very high melting point (2740 K). Attempts to prepare samples of Ce-activated Lu₂O₃ in the form of fibers have been made using the laser-heated pedestal growth technique; for a discussion of their optical properties we defer to reports presented elsewhere in these proceedings.[7] The properties of an additional high density oxide and of an oxysulfide of potential interest are included in Table 1, however no samples were available to test. A broad red emission from Ce³⁺ in the oxysulfide Lu₂O₂S has been reported at temperatures <170 K.[8] Thermal quenching of the luminescence at higher temperatures limits the usefulness of this material.

Table 1. Properties of high density Ce^{3+} hosts for 511 keV photons.

Compound	Crystal system	Density (g/cm ³)	Attenuation length (cm)	Photoelectric fraction (%)	Photoelectric length (cm)
Lu_2O_3	cubic	9.4	0.93	38.1	2.43
LuLaO_3	orthorhombic	8.2	1.17	31.7	3.68
$\text{Lu}_2\text{O}_2\text{S}$	hexagonal	8.9	0.99	37.0	2.67
$\text{Lu}_3\text{Al}_5\text{O}_{12}$ (3:5)	cubic (garnet)	6.7	1.41	29.0	4.87
LuAlO_3 (1:1)	orthorhombic	8.4	1.10	32.1	3.44
$\text{Lu}_4\text{Al}_2\text{O}_9$ (2:1)	monoclinic	~8.5	1.06	34.9	3.04
Lu_3BO_6 (3:1)	monoclinic	7.4	1.20	41.3	3.28
LuBO_3 (1:1)	hexagonal	6.9	1.32	37.2	3.91
LuTaO_4 (1:1)	monoclinic	9.8	0.90	37.8	2.37
Lu_3TaO_7 (3:1)	cubic	~10	~0.87	~39	~2.3
$\text{LuPb}_2\text{TaO}_6$	orthorhombic	10.1	0.77	45	1.70
LaTaO_4 (1:1)	monoclinic	7.8	1.22	31.6	3.86
LaTa_3O_9 (1:3)	tetragonal	8.1	1.12	34.8	3.21
$\text{LaTa}_5\text{O}_{14}$ (1:5)	orthorhombic	8.2	1.09	35.7	3.04
$\text{LaTa}_7\text{O}_{19}$ (1:7)	orthorhombic	8.3	1.07	36.2	2.72
$\text{Bi}_4\text{Ge}_3\text{O}_{12}$	cubic	7.1	1.21	46.0	2.63
LuF_3	orthorhombic	8.3	1.10	34.2	3.22
$\text{Lu}_3\text{KF}_{10}$	cubic	6.9	1.39	30.7	4.51
BaLu_2F_8	monoclinic	6.9	1.35	32.2	4.18

LUTETIUM ALUMINATES

The properties of three compounds of the lutetium oxide-aluminum oxide system are included in Table 1. Of these, the cubic garnet phase can be grown most easily. Obtaining the more dense perovskite phase free of the garnet phase requires more care.[8] As evident from several papers in this volume, the orthoaluminate LuAlO_3 has been the subject of intense study.

We have investigated the slightly more dense 2:1 compound $\text{Lu}_4\text{Al}_2\text{O}_9$. A sample was grown by Airtron from a stoichiometric melt doped with 0.75 at.% Ce using the Czochralski technique. The growth was well behaved but the single crystal decomposed during cooling. The x-ray pattern indicated that it was not single phase and Lu_2O_3 was also present. The x-ray excited decay could be fitted with three components having time constants and percentages of 0.3 ns (12%), 3.3 ns (22%), and 45 ns (66%). The intensity was less than that of BGO.

LUTETIUM BORATES

Properties of two lutetium borates are presented in Table 1. A powdered sample of the 1:1 compound LuBO_3 doped with 1% Ce was prepared by D. Keszler (Oregon State University)

and exhibited good light output (greater than that of BGO) and decay kinetics characterized by 4 ns (9.2%), 28 ns (32%), 335 ns (59%). This is a promising compound. It undergoes a phase transition at 1310 °C from the calcite to the valerite-type structure. Thus far we have been unable to obtain a good sample of the more dense 3:1 compound Lu_3BO_6 . An x-ray pattern attributable to this phase was obtained but was contaminated with other compounds.

TANTALATES

The properties of several Lu and La tantalates are given in Table 1. LuTaO_4 is a known phosphor material with an absorption peak at about 220 nm and intense emission at 330 nm arising from a charge transfer transition of the TaO_6 group. It has also been doped with Nb or Bi for emission at longer wavelengths [9,10] and with several trivalent lanthanide ions.[11] Varying relative amounts of tantalate and dopant emissions are observed and depend on the specific transitions involved. We have measured an x-ray excited decay time of 1.87 μs for a pure LuTaO_4 powder sample. A polycrystalline sample doped with 0.5% Ce grown from the melt by B. Chai (CREOL) exhibited a weak luminescence (less than BGO) with a decay that could be fitted approximately by three time constants of 59 ns (6%), 344 (27%), and 1.03 μs (67%). Powdered samples of $\text{LuTaO}_4\text{:Ce}$ prepared by C. Torardi (Du Pont) in a reducing atmosphere to minimize the presence of Ce^{4+} also exhibited a weak scintillation output; for the most concentrated sample (3% Ce) the output was very weak and fast. All samples had a pale yellow coloration. Samples of the more dense 3:1 compound Lu_3TaO_7 do not luminesce under x-ray excitation [12]; no Ce-doped samples of this compound or the ultra-dense lutetium-lead tantalate in Table 1 have been prepared.

The lanthanum tantalates are not as dense as the lutetium compounds but the La site is a much better size fit for Ce than Lu. The absorption edge of LaTaO_4 is at 260 nm. Luminescence associated with the tantalate group has been observed at low temperatures (77 K) [10]; only weak x-ray excited luminescence is observed at 300 K.[12] Luminescence has been reported for LaTaO_4 doped with Eu^{3+} and Tb^{3+} with little transfer from the tantalate group evident from excitation spectrum.[13] A polycrystalline sample of LaTaO_4 doped with 0.2% Ce exhibited a decay of 1.8 ns (61%) and 75 ns (39%). This material undergoes a phase transition at 600 °C. Corresponding decays from a polycrystalline 0.5% Ce sample of the more dense LaTa_3O_9 were 1.7 ns (29%) and 35.3 (71%). This material melts at 1850 °C and shows no phase transition during cooling. Neither compound exhibited strong scintillation output (< BGO).

BISMUTH GERMANATE

$\text{Bi}_4\text{Ge}_3\text{O}_{12}$ (BGO), while not as dense as some of the other materials in Table 1, is of interest because it has a smaller photoelectric length than most of the other materials. Several trivalent lanthanide ions have been added to BGO in small quantities (< 1 at.%) for studies of spectroscopic and defect properties and to increase radiation stability.[14] BGO has the eulytite structure; intense UV-excited Ce^{3+} luminescence has been reported from several phosphate-containing eulytites, e.g., $\text{Sr}_3\text{La}(\text{PO}_4)_3$. [15] The fundamental band gap of BGO is near that expected for the Ce^{3+} 4f–5d splitting. The large Stokes shift of the BGO emission, however, is unfavorable for energy migration to Ce. A crystal doped with a nominal 0.2% Ce was measured and exhibited an initial decay component (~20%) having a lifetime of ~30 ns in addition to the ~300 ns decay observed in undoped BGO. The total light output from this

sample was reduced slightly with respect to that of undoped BGO. Growth in a reducing environment is required to minimize the formation of Ce^{4+} .

LUTETIUM FLUORIDES

The properties of several Lu fluorides are included at the bottom of Table 1. LuF_3 is attractive from the viewpoint of density but is difficult to prepare. Samples of $BaLu_2F_8$ were prepared by B.Sobellov (Institute of Crystallography). Undoped $BaLu_2F_8$ exhibits a very fast luminescence which is believed to be due to a core-valence transition associated with Ba; the decay time was 0.86 ns. The scintillation light was about one-third of that of BaF_2 , which is reasonable in view of the smaller cation percentage of Ba. A sample of $BaLu_2F_8$ doped with 3% Ce had an x-ray excited decay characterized by two components: 6.3 ns (28%) and 39 ns (72%). The rise time of the Ce luminescence was consistent with radiative transfer of cross luminescence from the host.

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